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PREPARATION OF ISONITRILE-SUBSTITUTED GROUP VI METAL CARBONYLS BY PHASE-TRANSFER CATALYSIS

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Summary

The substitution of Group VI metal carbonyls by t-butyl isonitrile or *p*-tolyl isonitrile using a benzene/50% aqueous sodium hydroxide two-phase system and a phase transfer catalyst at 20°C is a convenient high yield synthetic route to the mono-substituted complexes, $[M(CO)_5(CNR)]$ (M = Cr, Mo, W). Disubstituted complexes *cis*-$[M(CO)_4(CNR)_2]$ (M = Mo, W) can also be prepared

Isonitrile substituted Group VI metal carbonyls $[M(CO)_x(CNR)_{6-x}]$ (M = Cr, Mo or W; x = 1—5; R = alkyl or aryl) have been much studied and several methods have been used in their synthesis. Direct, thermal substitution of a metal carbonyl can be slow e.g. treatment of $[Cr(CO)_6]$ with t-BuNC at 100°C for 48 hours gave $[Cr(CO)_5(CNt\text{-}Bu)]$ but in only 7% yield [1]. Since some isonitriles are not thermally stable this is not a good method. A better method is to first prepare a halo(pentacarbonyl)metal anion e.g. as a salt such as $Et_4N[M(CO)_5X]$ (M = Cr, Mo or W; X = Cl, Br or I) and to treat this with the isonitrile: substitution occurs at room temperature [1—3]. Various olefin- or nitrile-substituted Group VI metal carbonyls have also been treated with isonitriles to give di-, tri- or tetra-substitution i.e. compounds of type $[M(CO)_x(CNR)_{6-n}]$ (x = 2, 3 or 4) [2,3]. Carbonylation of $[Cr(CNR)_6]$ has also been used but gives poor yields: better yields are obtained by heating mixtures of $[Cr(CO)_6]$ and $[Cr(CNR)_6]$ in a sealed tube [4]. Isonitrile substituted Group VI metal carbonyls have also been synthesized from thiocarbonyl complexes [5] and also from arenediazonium pentacarbonyl complexes [6].

We have shown that the substitution of Group VI metal carbonyls by tertiary phosphines, triphenylarsine or dipyridyl is greatly accelerated by hydroxide ion under phase-transfer conditions [7]. Isonitriles are stable to strong alkali and we now show that this phase-transfer method can be used as the basis of a convenient method of synthesizing mono-substituted derivatives $[M(CO)_5(CNR)]$, and to a lesser extent the di-substituted derivatives *cis*-$[M(CO)_4(CNR)_2]$. We have now used t-butyl isonitrile and *p*-tolyl isonitrile as typical examples of an aliphatic

TABLE 1

REACTANTS, PRODUCTS AND CONDITIONS [a] FOR THE SYNTHESIS OF ISONITRILESUBSTITUTED GROUP VI METAL CARBONYLS IN THE TWO-PHASE BENZENE/50% SODIUM HYDROXIDE SYSTEM

Hexa-carbonyl	Ligand RNC, R =	Mol. Ratio RNC/M	Reaction time (h)	Products (yield, %) [b]	
Cr	t-Bu	1.03	1	$[Cr(CO)_5(CNt\text{-}Bu)]$	(81)
Mo	t-Bu	1.03	1	$[Mo(CO)_5(CNt\text{-}Bu)]$ *cis*-$[Mo(CO)_4(CNt\text{-}Bu)_2]$	(54) (18)
W	t-Bu	1.03	1	$[W(CO)_5(CNt\text{-}Bu)]$ (70) *cis*-$[W(CO)_4(CNt\text{-}Bu)_2]$	(70) (15)
Mo [c]	t-Bu	3.3	1	$[Mo(CO)_5(CNt\text{-}Bu)]$ (50) *cis*-$[Mo(CO)_4(CNt\text{-}Bu)]$	(50) (37)
Mo	t-Bu	1.03	10 min	$[M(CO)_5(CNt\text{-}Bu)]$ (59) *cis*-$[Mo(CO)_4(CNt\text{-}Bu)_2]$	(59) (6)
Cr	*p*-Tol	1.03	1	$[Cr(CO)_5(CNC_7H_7)]$	(81)
Mo	*p*-Tol	1.03	1	$[Mo(CO)_5(CNC_7H_7)]$ *cis*-$[Mo(CO)_4(CNC_7H_7)_2]$	(57) (20)
W	*p*-Tol	1.03	1	$[W(CO)_5(CNC_7H_7)]$ (59) *cis*-$[W(CO)_4(CNC_7H_7)_2]$	(59) (20)

[a] At ca. 20°C, unless stated otherwise. [b] Based on the metal carbonyl not on the isonitrile. [c] At 65—70°C.

and an aromatic isonitrile. Thus treatment of chromium hexacarbonyl in benzene with t-butyl isonitrile and 50% aqueous sodium hydroxide using benzyl(triethyl)ammonium chloride as phase-transfer catalyst gave after 1 hour at 20°C the mono-substituted product $[Cr(CO)_5(CNt\text{-}Bu)]$ in 81% yield. No di-substituted product could be detected. Similar treatments of molybdenum or tungsten hexacarbonyls gave mainly the mono-substituted product $[M(CO)_5(CNt\text{-}Bu)]$ together with some di-substituted *cis*-$[M(CO)_4(CNt\text{-}Bu)_2]$. The method is described in more detail in the Experimental and in Table 1. Compounds of the type $[M(CO)_5(CNt\text{-}Bu)]$ and *cis*-$[M(CO)_4(CNt\text{-}Bu)_2]$ were readily separated by sublimation under vacuum when at ca. 90°C and 20—25 mm only the mono-substituted sublime. They were identified by their published IR spectral data {values of ν(CO) and ν(CN)} in *n*-hexane solution, by their melting points and by their proton NMR spectra [2,3]. Treatment of molybdenum hexacarbonyl with an excess of t-butyl isonitrile (3.3 mole per molybdenum) under the phase transfer conditions but at a higher temperature (65—70°C) still gave $[Mo(CO)_5(CNt\text{-}Bu)]$ as the major product (50% yield) but *cis*-$[Mo(CO)_4(CNt\text{-}Bu)_2]$ was also isolated in 37% yield. The behaviour towards *p*-tolyl isonitrile paralleled that towards t-butyl isocyanide in that chromium hexacarbonyl gave only the monosubstituted compound but molybdenum and tungsten gave mixtures of the mono- and di-substituted complexes (Table 1): these were readily separated by sublimation at 90°C 0.1 mm and identified from their published melting point and spectral data. The tungsten complexes are new and were formed in very high total yield (Table 1). Characterizing data for these tungsten complexes are given in the Experimental.

Experimental

Melting points were determined on a Kofler hot-stage apparatus and are corrected. IR spectra were determined on a Perkin-Elmer R257 (4000—400 cm^{-1}) spectrometer. ^{1}H NMR spectra were determined on a Perkin Elmer R12 spectrometer. A typical preparation is given below: the reaction conditions and yields etc. for other preparations are shown in Table 1.

Pentacarbonyl{t-butyl isocyanide}molybdenum(0) and tetracarbonylbis{t-butyl isocyanide}molybdenum(0). A mixture of molybdenum hexacarbonyl (1.48 g, 5.61 mmol), t-butyl isonitrile (0.481 g, 5.78 mmol) benzene (80 cm^3), 50% aqueous sodium hydroxide solution (18 cm^3) and benzyl(triethyl)ammonium chloride (82 mg) was stirred vigorously at ca. 20°C for 1 h under argon. Water (ca. 50 cm^3) was then added and the organic layer separated, dried ($MgSO_4$) and evaporated. The residue was heated in a sublimation apparatus (ca. 90°C/25 mm) when [$Mo(CO)_5(CNt\text{-}Bu)$] was collected on a cold finger. Yield (0.967 g, 3.03 mmole, 54%). The residue was recrystallized from dichloromethane/hexane to give *cis*-[$Mo(CO)_4(CNt\text{-}Bu)_2$] (0.373 g, 0.995 mmol, 18% yield).

[$W(CO)_5(CNC_7H_7)$] was obtained as white prisms, m.p. 136—138°C. Found: C, 35.65; H, 1.5; N, 3.2. $C_{13}H_7NO_5W$ calcd.: C, 35.40; H, 1.65; N, 3.2%. I.R. data (in hexane) ν(CO) 2059, 1983, 1959 and 1928 cm^{-1}. ν(CN) 2140 cm^{-1}.

[$W(CO)_4(CNC_7H_7)_2$] formed yellow prisms, m.p. 162—163°C. Found: C, 44.95; H, 2.75; N, 5.3 $C_{20}H_{14}N_2O_4W$ Calcd.: C, 45.30; H, 2.66; N, 5.3%. I.R. data ν(CO) (in hexane) 2012, 1932, 1924 and 1920 cm^{-1} ν(CN) (in CH_2Cl_2) 2162 and 2130 cm^{-1}.

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